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# Phosphorous recovery from sewage sludge ash suspended in water in a two-compartment electrodialytic cell

*Lisbeth M. Ottosen\*, Pernille E. Jensen, Gunvor M. Kirkelund*

Department of Civil Engineering, Brovej, Building 118, Technical University of Denmark, 2800 Kgs.

Lyngby, Denmark. \*LO@byg.dtu.dk

## ABSTRACT

Phosphorus (P) is indispensable for all forms of life on Earth and as P is a finite resource, it is highly important to increase recovery of P from secondary resources. This investigation is focused on P recovery from sewage sludge ash (SSA) by a two-compartment electrodialytic separation (EDS) technique. Two SSA are included in the investigation and they contained slightly less P than phosphate rock used in commercial fertilizer production and more heavy metals. The two-compartment electrodialytic technique enabled simultaneous recovery of P and separation of heavy metals. During EDS the SSA was suspended in water in the anolyte, which was separated from the catholyte by a cation exchange membrane. Electrolysis at the anode acidified the SSA suspension, and hereby P, Cu, Pb, Cd and Zn were extracted. The heavy metal ions electromigrated into the catholyte and were thus separated from the filtrate with P.

More than 95% P was extracted from both SSAs. The charge transfer to obtain this varied when treating the two SSAs, and for one ash it was about 30% higher than for the other as result of a higher buffering capacity against acidification. The repeatability of EDS results between experiments with the same SSA and the same experimental conditions was good, which shows that the process is easy to control at the studied laboratory conditions. About 80% P and 10% of the heavy metals remained in the filtrate from the anolyte after treatment of both SSAs. The heavy metal content relative to P in the filtrate by far meet the limiting values for use of industrial wastes as fertilizers, thus the filtrate is ready for direct processing into P-fertilizer.

## **1. INTRODUCTION**

By the human perspective, resources are non-renewable when their rate of consumption exceeds the rate of recovery. Depletion of P from primary sources is a result of non-sustainable use. It is time to acknowledge the reality of the finite limit and develop methods for recovery of P from secondary sources. One such source is ash from incineration of sewage sludge (SSA). Sewage sludge incineration is a well proven technology with hundreds of plants worldwide (Werther and Ogada, 1999); 1.7 million tonnes of SSA are produced annually world-wide, and the production is likely to increase in the future (Donatello & Cheeseman 2013). The concentration of P in SSA is generally 5-10% (Cyr et al. 2007), thus approaching the content in virgin phosphorite, which indicates that SSA is a significant potential secondary P resource. There is limited gain in crop yield if SSA is spread directly at agricultural land as P is not in a plant available form in the ash. In addition, heavy metals are concentrated in the SSA during incineration, which prohibits use of SSA in agriculture.

Different techniques are under development for recovery of P from SSA. The techniques can be grouped in two: thermochemical treatment or chemical extraction. These methods are reviewed in (Donatello & Cheeseman 2013). Current practice for handling the SSA from the two Danish plants, from where ash was sampled for the present investigation, is landfilled in special landfills with only SSA. The purpose is to recover the P from the landfilled ashes, when proper and economical methods have been developed. This work updates the technology where the P is extracted in acid. A major problem with acid extraction is the simultaneous extraction of heavy metals and P (Donatello et al. 2010a; Ottosen et al. 2013). In order to obtain a clean P product, various processes for separation of P and heavy metals have been suggested: pH adjustment (Franz 2008, Takahashi 2001), sulfide precipitation (Franz, 2008), cation exchange (Franz, 2008; Donatello et al. 2010b) and electrodialytic separation (Ottosen et al. 2014, Guedes et al. 2014, Ebbers et al. 2014a). The first three separation techniques require a two-step treatment, first P extraction and subsequent separation. In electrodialytic separation the P extraction and heavy metal separation occur simultaneously. The present paper focus on electrodialytic separation and reports laboratory tests with two-compartment electrodialytic P recovery from sewage sludge ash from incineration of municipal wastewater sludge. A major focus is on describing the major elements and heavy metal content of the recovered P and comparing it to commercial P-fertilizers. The ashes originate from the two (out of three) largest sewage sludge incineration plants in Denmark as it is interesting to investigate the robustness of EDS method for ashes from both plants.

## **1.1 Two-compartment EDS**

The principle of the two-compartment EDS setup used in this paper is illustrated in figure 1. The major objective with this setup is a simultaneous extraction of P and removal of heavy metals from the liquid with P. When the electrical DC current is applied to the electrodes, the SSA suspension will gradually be

acidified due to electrolysis at the anode ( $\text{H}_2\text{O} \rightarrow 2\text{H}^+ + \frac{1}{2}\text{O}_2(\text{g}) + 2\text{e}^-$ ). During the acidification heavy metals and P are extracted from the ash. The heavy metals are transported by electromigration over the cation exchange membrane (CEM) and concentrate in the cathode compartment. The extracted P remains in the filtrate of the ash suspension. Hereby simultaneous extraction and separation is obtained.

A two-compartment electrodialytic setup has previously been tested for purification of wet industrial phosphoric acid (Touaibia et al. 1996), but this setup was opposite to the one of this paper. In (Touaibia et al. 1996) the two compartments were separated by an anion exchange membrane (AEM) and the phosphoric acid to be treated was placed in the cathode compartment. Here the impurities were retained in the catholyte and P electromigrated to the anolyte where phosphoric acid was formed with protons produced by the anodic electrolysis. The concentration of the phosphoric acid produced by this method was, however, limited by proton leakage through the AEM (Touaibia et al. 1996). The two compartment system with the cathode placed in reject water from a WWWT plant and separation of P into the anolyte was tested in (Ebberts et al. 2015b), however, the increase in pH caused P precipitation and limited the recovery. A three compartment EDS system based on the idea of recovering phosphoric acid in the anolyte and heavy metals in the catholyte was tested by Ottosen et al. (2014) and by Guedes et al (2014). These works, however, showed that the transport of P into the anolyte was inefficient. Phosphorous has four speciation steps:  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$  and  $\text{PO}_4^{3-}$  and the corresponding acid constants ( $\text{pK}_a$ , 298 K) are 2.12; 7.2 and 12. Thus at pH less than 2, P is present as phosphoric acid without any charge and thus not mobile for electromigration. But at the same time pH needs to be less than 2 to fully extract P from SSA (Ottosen et al. 2013). Contrarily, the heavy metal transport into the catholyte progressed well in the three compartment electrodialytic cell, as heavy metals are present in ionic form as released from the SSA by acid (Ottosen et al 2014). The insufficient P recovery in the anode compartment using the

three compartment EDS cell formed basis for the idea of a simpler setup; the two compartment EDS cell. The overall idea of the two-compartment EDS is to keep the P in the filtrate to which it is extracted and transport the heavy metals out from this filtrate in the applied electric field. By placing the anode directly in the suspension a faster acidification and subsequent release of P and heavy metals is obtained compared to the three compartment cell.

Phosphorous extraction in two-compartment EDS was experimentally compared to three-compartment EDS (Ebberts et al. 2014a) where experiments were made with ash suspended in distilled water or  $\text{H}_2\text{SO}_4$ . The fastest recovery of P was obtained in the two-compartment cell when the SSA was suspended in  $\text{H}_2\text{SO}_4$ . However, when suspending the ash in  $\text{H}_2\text{SO}_4$  gypsum was formed by  $\text{Ca}^{2+}$  released from the ash and the  $\text{SO}_4^{2-}$  from the acid (Ottosen et al. 2014). The formation of gypsum increases the volume of particulate matter to be landfilled. Environmentally as well as economically it would be beneficial to use the remaining ash in e.g. construction materials rather than landfilling. SSA has been suggested to be used in different construction materials. Donatello & Chesemann (2013) reviewed the use in: sintered ceramics (bricks and lightweight aggregates) and in concrete as cement replacement or in the production of the cement. The gypsum formation may hamper such use. Also other anions, such as  $\text{Cl}^-$  or  $\text{NO}_3^-$  added by use of other mineral acids for P dissolution may impede the use of the residual ash in construction materials and they will be impurities in the phosphoric acid. This problem is completely avoided by the use of EDS and acidification thorough electrolysis at the anode. For use in concrete, milling of SSA showed very beneficial due to improved pozzolanic activity (Donatello et al. 2010a). For this reason and because the finer particle size after milling eased keeping the ash suspended during EDS, the SSA was milled prior to treatment in the present work. Experiments were conducted with SSA's from two different incineration plants. We investigated and compared the recovery of P from the two SSAs and the

separation of heavy metals from the filtrate into the catholyte. Finally the purity of a phosphorous salt produced from evaporation the water from the filtrate was evaluated.

## **2. MATERIALS AND METHODS**

### **2.1 Experimental ashes**

SSAs from the two major Danish mono-incineration plants were used. The sludge incinerated at both plants originated from municipal wastewater treatment. Iron was used in both waste water facilities to precipitate P, and the sewage sludge was incinerated in a fluidized bed combustor at about 850°C. Ash A was sampled at Spildevandscenter Avedøre and ash B was from Lynettefællesskabet. Both ashes were sampled directly from ash silos when the ash was filled in trucks for transportation away from the plants. Ash A was sampled as a mix of electrofilter ash and bag filter ash (2%), whereas ash B was sampled directly after the electrofilter. After sampling, the ashes were stored in closed plastic containers at room temperature. Before use, the ashes were milled for 30 seconds in a Vibrating Cup Mill PULVERISETTE 9.

### **2.2 Analytical and ash characterization**

Characterization was made with dried ash (105°C, 24 hours). Concentrations of P, Cu, Pb, Zn and Cd were measured in all samples with a Varian 720-ES ICP-OES (Inductively Coupled Plasma - Optical Emission Spectrometry). SSA samples were pre-treated in accordance to Danish Standard DS259: 1.0 g ash and 20.0 ml (1:1) HNO<sub>3</sub> was heated at 200 kPa (120°C) for 30 minutes and filtered through a 0.45 µm filter prior to the analysis by ICP-OES. Ash pH and conductivity were measured after suspending 10.0 g ash in 25 ml distilled water. After 1 hour agitation pH and conductivity were measured directly in

the suspension with Radiometer electrodes. Water content was measured as weight loss after 24 hours at 105°C (calculated as weight loss over the weight of the wet sample). Loss on ignition (LoI) was found after 30 minutes at 550°C. Five duplicates of each of these analyses were made. Solubility in water was evaluated: 50.0 g ash suspended in 500 ml distilled water and agitated for 1 min. After settling the water was decanted. New 500 ml distilled water added. This was repeated so the ash was washed three times. Finally the suspension was filtered and the ash dried and weighed.

### **2.3 Experiments with two-compartment electro dialytic P recovery**

The experiments were conducted in a cylindrical cell as shown in figure 1. The length of the anode compartment with ash suspension was 10 cm and the length of the cathode compartment 5 cm. The internal diameter of both compartments was 8 cm. The cation exchange membrane was from Ionics (CR67 HUY N12116B). The electrodes were made of platinum coated titanium wire (diameter 3 mm) obtained from Permascand®) and the length of the electrode in the catolyte was approximately 4 cm. A power supply (Hewlett Packard E3612A) was used to maintain a constant current of 50 mA. The SSA was kept suspended in the anode compartment by an overhead stirrer (RW11 basic from IKA). In the cathode compartment 500 mL 0.01 M NaNO<sub>3</sub> adjusted to pH 2 with HNO<sub>3</sub> was circulated. The circulation of the catolyte ensures a continuous flow in this compartment and prevents build-up of high concentration gradients at the surface of the cation exchange membrane and it flushes the produced H<sub>2</sub> gas from electrolysis out of the compartment. During experiments, pH was adjusted manually in the cathode compartment to between 1 and 2 daily with 1 M HNO<sub>3</sub>. Conductivity and pH in the ash suspension and voltage between electrodes were also measured daily.



Totally 12 EDS experiments were made with duration and type of SSA as the two varying parameters (see table 1). In every experiment 25 g SSA was suspended in 350 ml distilled water (corresponding to a liquid to solid ratio L:S = 14). Three identical experiments A4-A6 were conducted to investigate the repeatability of the results.

160

At the end of the EDS experiments the suspension was filtered at atmospheric pressure. Contents of P, Cu, Zn, Pb and Cd were measured in the ash, solutions, cation exchange membrane and on the cathode. The ash was dried before measurement of the same chemical elements (triplicate measurements). The contents in the cation exchange membrane were measured after extraction in 1.0 M HNO<sub>3</sub> and rinsing of the electrodes prior to measurement was done in 5.0 M HNO<sub>3</sub>. For further investigating the purity of the P produced, the filtrate from experiment A6 was placed in an oven at 50°C in order to evaporate the water and produce a salt. As shown later the P extraction had reached maximum in experiment A6 and this was the reason for choosing it. The purpose was twofold: to analyze the concentration of heavy metals in relation to P and to evaluate the quality of the produced salt as basis for P fertilizer. The produced salt was stored in a desiccator to hinder hygroscopic uptake of moisture from the air. The salt was characterized by the total content of macro elements (P, Ca, Fe and Al), heavy metals (Cu, Pb, Zn and Cd) after DS259 (described above). It was checked that the macro elements analyzed were those present in the salt by elemental mapping of the salt crystals using Scanning Electron Microscopy with Energy Dispersive X-Ray Analysis (SEM-EDX). The water soluble fraction in the salt of the same elements extracted in distilled water at liquid to solid ratio (L:S) 2.5 was measured as well.

### 3. RESULTS AND DISCUSSION

#### 3.1 The SSAs as secondary P resource

178 Characteristics of the SSAs are shown in table 2. Both ashes were alkaline, but Ash A had lower pH (pH  
179 9.5) than Ash B (pH 12.4). Ash B contained a larger water soluble fraction than ash A, seen from both  
180 the higher water soluble fraction and the higher conductivity when suspended in water.

181

182 It is interesting to compare the SSAs as being secondary resources for P to the primary resource being  
183 the phosphate rock. Phosphorus pentoxide ( $P_2O_5$ ) is the commonly reported constituent of the phosphate  
184 rock. The economic grade of phosphate rock varies from 25% to 37%  $P_2O_5$  (Gupta et al 2014). This  
185 concentration range corresponds to 110-160 g P/kg phosphate rock and thus the P concentration in SSA-  
186 A (110 g/kg) is exactly at the lower end of this range, but the concentration in SSA-B (73 g/kg) is lower.  
187 The concentrations in the SSAs are though high enough to be considered as secondary P resources. Ores  
188 of the phosphorous rock contain various toxic metals and radionuclides which later are transferred to  
189 phosphate fertilizers (Gupta et al. 2014). The concentrations Cu, Zn and Pb in different phosphate rock  
190 for production of fertilizer were compiled by (Aydin et al 2010), and the ranges reported were 6-130 mg  
191 Cu/kg, 6-515 mg Zn/kg and 4-455, 93-2060 mg Pb/kg, 0.1 – 60 mg Cd/kg. The heavy metal  
192 concentrations reported in literature in different SSAs were collected in (Cyr et al 2007): 200-5400 mg  
193 Cu/kg; 1080-10,000 mg Zn/kg, 93-2060 mg Pb/kg and 4-94 mg Cd/kg. In general Zn and Cu  
194 concentrations in SSAs are thus higher than in phosphate rock, Pb concentrations are overlapping in the  
195 high range of phosphate rocks and low range of SSA. The concentration ranges are overlapping in the  
196 case of Cd, though higher Cd concentrations were found in the SSAs. The ashes of the present  
197 investigation follow this general trend, yet the heavy metal concentration is low. The concentrations in  
198 the two SSAs of the present investigation fall within the lower ends of these ranges for heavy metals in  
199 SSA except for Pb in SSA-B and Cd in both ashes, which are even lower than the lowest concentration  
200 previously reported. In summary, the SSAs contained slightly less P than phosphate rock used in

201 commercial fertilizer production and more heavy metals. The heavy metals in P fertilizer are taken up by  
202 the crops (Gupta et al. 2014) and if the P related heavy metal concentration in SSA is not reduced, this  
203 issue causes concern in the use of SSA as resource for P fertilizer. Thus separation of P and heavy metals  
204 from SSA is important.

205

### 206 **3.2 EDS process repeatability**

207 Acceptable mass balances (defined as mass of an element in the different parts at the end of the  
208 experiment over the mass of the element initially in the ash) were obtained for P, Cu, Zn and Pb in every  
209 experiment (90-110%), whereas for Cd, the mass balances were not this good due to a low initial  
210 concentration. Subsequently only the distributions for Cu, Zn and Pb from the EDS experiments are  
211 given. The content of Cd in the final P product is discussed on basis of the produced salt later.

212

213 The repeatability of EDS experiments can be evaluated by comparing the three identical experiments  
214 with SSA-A and the duration 10 days (A4 to A6). In each of these three experiments about 54% ash was  
215 dissolved during the treatment and final pH of the suspension was 1.1 (table 1). The distribution of P,  
216 Cu, Pb and Zn in ash, filtrate and cathode compartment (cation exchange membrane, catolyte and at the  
217 cathode) are shown in figure 2. The average values are given with error bars showing minimum and  
218 maximum values. The separation results were very similar for the three experiments and the deviation  
219 from the average value was 5% or less. Almost all P was extracted, and only 2-3% remained in the ash  
220 at the end of the experiments. Around 80% P was found in the filtrate of the suspension. Also for each  
221 of the heavy metals the distributions are the same. For Cu and Zn the major parts are found in the cathode  
222 compartment (>70%) whereas 60% Pb remained in the ash. On the basis of the very similar result

obtained in these experiments A4-A6 it was decided to make the remaining experiments of the investigation as single experiments.

### 3.3 Optimal duration of EDS for P recovery

The development in distribution of P, Zn, Pb and Cu as result of the EDS duration is seen in figure 3 (SSA-A) and figure 4 (SSA-B). The general trend between the two ashes is a slower extraction of all four elements from SSA-B. During the first 5 days less than 10% of each element was released from SSA-B, whereas about 80% P; 65% Zn and Cu; and 10% Pb were released from SSA-A. This corresponds to the faster acidification of the suspension with SSA-A and faster ash dissolution (table 1). This is in accordance with previous findings, as release of both P and heavy metals from SSA was shown to increase with decreasing pH (Ottosen et al. 2013, Donatello et al. 2010). It was also previously shown that different SSAs have different buffering capacities and require different amounts of acid for P extraction (Ottosen et al. 2013) and this was also the case for the two present ashes even if they are both from fluidized bed incineration of Fe rich ash at about 850°C.

Almost all P (>95%) was extracted between 5-7 days of EDS of SSA-A and between 7-10 days of SSA-B (figures 3 and 4). The P extraction corresponds to the time where pH reaches below 2 (table 1), which again corresponds to the finding for SSA-A, reported in (Ottosen et al. 2013) for chemical extraction in HNO<sub>3</sub> where 50-60% P was extracted at pH 2 and 85-100% P at pH of about 1 from this ash. Results with two-compartment EDS was reported in (Ebberts et al 2015a) with SSA from the same plant as SSA-A of the present investigation but with lower L:S (10 vs. 14) and the same current. The lower L:S prolonged the extraction time slightly as the buffering capacity of the suspension increases with ash amount. In (Ebberts et al 2015a) about 80% P was extracted during 7 days.

246 For both SSAs prolonging EDS after the time where full P extraction was obtained meant a loss of P into  
247 the cathode compartment (figures 3(d) and 4(d)). After 14 days of EDS the lost P was approximately  
248 18% for both ashes. When terminating the experiments at the point where maximum P extraction is  
249 obtained the loss of P into the cathode compartment is about 10% from both ashes and this loss seem  
250 hard to hinder. As the two compartments are separated by a CEM, which hinder transport of anions, the  
251 P transported into the catholyte may have been transported as neutrally charged complexes by diffusion  
252 due to the concentration difference in the two compartments or by electromigration as cationic species  
253 may be formed e.g. from the reactions:  $\text{Al}^{3+} + \text{H}_2\text{PO}_4^- \rightarrow \text{AlH}_2\text{PO}_4^{2+}$  or  $\text{Al}^{3+} + \text{H}_2\text{PO}_4^{2-} \rightarrow \text{AlH}_2\text{PO}_4^+$   
254 (Nordstrom & May, 1989). During the two experiments with duration of 14 days A7 and B4, 45% and  
255 32% Al was transported into the cathode compartment, respectively, and it is possible that some of the  
256 Al had formed positively charged complexes with P.

257 Incineration of sewage sludge is used worldwide, but an emerging technology is low-temperature  
258 gasification, which allows energy production from biomass resources like sewage sludge with high  
259 contents of low melting point ash compounds, which can cause boiler operational problems in the more  
260 traditional incineration (Skoglund et al. 2013). Viader et al. (2015) tested two compartment EDS (at L:S  
261 10 and an applied current of 50 mA) from ash from gasification of two different municipal sewage  
262 sludges from a plant where P was captured 50% biologically and 50% chemically (with Fe and Al  
263 chlorides) and a plant where P was mainly removed biologically with a minor amount of Fe salts (this  
264 latter was co-gasified with wheat straw pellets). During 7 days 26% and 90% P was recovered by EDS,  
265 respectively. The low P-extraction from the first ash was suggested being due to low-soluble Fe-  
266 phosphates formed during the gasification. This hypothesis is supported by the good EDS result from the  
267 other ash, with only a minor content of Fe. Even though the SSA from the present investigation originates  
268 from sludge where Fe-salts were used for P precipitation, the EDS extraction of P is not hampered by

269 this, probably because iron oxides are formed during incineration rather than iron phosphates, so the  
270 choice of thermal process influences P extractability from the ash. The possible EDS for extraction of P  
271 and separation of heavy metals from SSA was shown being dependent on the precipitation chemicals  
272 used at the WWWT in (Ottosen et al 2014), so this is the case for both gasification and incineration ashes.

273

### 274 **3.4 Heavy metal removal**

275 As well as P, the heavy metals were mobilized faster from SSA-A than SSA-B (figures 3 and 4). The  
276 mobilization of Cu and Zn was faster than Pb from both ashes, i.e. Zn and Cu were mobilized at a higher  
277 pH. The nature and proportion of minerals controlling the mobilization behavior of the different heavy  
278 metals from sewage sludge ash have not yet been studied in-depth. The mineralogy in SSA represents an  
279 assemblage of crystalline and amorphous phases and it is a very complex system. However, the finding  
280 that Pb is mobilized to a lesser extent than Cu and Zn is in accordance to findings from chemical  
281 extraction in acid for SSAs (Ottosen et al. 2013), three compartment EDS (Ottosen et al 2014, Guedes et  
282 al. 2014), two-compartment EDS (Ebbens et al 2015a) and it is also a general finding using three-  
283 compartment EDS for treatment of different ash types e.g. municipal solid waste incinerator fly ash  
284 (Pedersen et al 2003) and wood ash (Ottosen et al 2007).

285

286 At day 10 the pH in both ash suspensions reached approximately 1 (table 2). At this point the mobilized  
287 percentages were:

288 SSA-A: 88% Cu, 42% Pb and 80% Zn

289 SSA-B: 41% Cu, 39% Pb and 29% Zn

290 After this point pH stabilized in both experimental series and the mobilization of the heavy metals  
291 stopped.

292

293 Jensen et al. (2006) reported remediation results for Pb from soil fines in a three-compartment  
294 electro dialytic cell. The distribution of Pb in the cell over time was reported in a similar way as figures  
295 3 and 4 in the present work. The work by Jensen et al. (2006) clearly illustrated how the removal of Pb  
296 underwent four phases:

- 297 (1) a “lag-phase”, where removal was substantially absent  
298 (2) a high removal rate involving dissolution of Pb into the soil solution  
299 (3) low removal rate, where the already dissolved Pb was removed from solution  
300 (4) no further Pb-removal was obtained as the treatment proceeded.

301 The same four phases can be used to describe the removal of the heavy metals from the SSAs in the  
302 present investigation. The “lag-phase” (1) is the phase until the buffering capacity of the ash is exceeded  
303 and the suspension reaches an acidification level, where the heavy metal is released (2). The duration of  
304 this phase was dependent on both the buffering capacity of the SSA and the actual heavy metal. The  
305 treatment should be finished by the end of phase (3) or at latest at the beginning of phase (4) because  
306 further treatment does not lead to any improvements but only increased energy consumption. In the actual  
307 experiments this point is related to the stabilized pH at about 1, after which the major current carrier will  
308 be H<sup>+</sup> ions. Similar phases are thus found during electro dialytic treatment of soil fines and sewage sludge  
309 ash. The focus in this investigation is recovery of P and simultaneous removal of heavy metals and it is  
310 important to finish the treatment to hinder significant loss of P into the catolyte.

311 The four phases are easiest distinguished for Cu and Zn in SSA-B (figure 4). Phase (1) is approximately  
312 5 days; Phase (2) between 5 and 7 days; Phase (3) is between 7 and 10 days, though not seen as a  
313 decreased removal rate compared to the previous phase, but only from the stop in heavy metal removal

of the already mobilized part, Phase (4) is after 10 days, where the distribution of Cu and Zn does not change over time. The phases have different durations for Cu and Zn in SSA-A (figure 3). Phase (1) was less than 3 days the change from phase (2) to (3) is around 5 days, as hereafter the concentration in the solution of the suspension decreases. This means that the removal rate in the applied electric field is faster than the rate with which heavy metal release from the ash occur. Phase (4) starts at about day 10. In relation to Pb both were within phase (3), even with the longest durations. The optimal duration at the conditions of the present investigation is about 7 days for Ash-A and 10 days for Ash-B. Distinguishing the separation process into these phases can be useful when optimizing EDS as the experimental conditions can be optimized for each phase.

### **3.5 The treated ash**

The concentrations of Cu, Pb and Zn in the ash decreased over time in Ash A while they increased in ash B during EDS (table 2). This distinct difference shows that whereas the heavy metals are found in relatively high concentrations in the soluble ash particles of Ash A (under conditions of EDS) they are found in the least soluble particles in Ash B. This underlines the different characteristics of the two SSAs even though they are both from mono-incineration of sewage sludge in fluidized bed at 850°C. The final concentrations of Cu and Zn were 3-4 times higher in Ash B after 14 days of EDS even though the initial concentration was lower. This might influence the possible uses of the ashes in construction materials, where high heavy metal concentrations can hamper the use.

### **3.6 Purity of the filtrate with P**

The salt produced from evaporation of the water from the filtrate in experiment A6 (where the extraction of P and separation of heavy metals had reached slightly into phase 4, i.e. the heavy metal cations are



337 transported into the catolyte) is evaluated in relation to the heavy metal concentrations by comparison to  
338 the limiting values for use of waste on agricultural land in Denmark (Miljøstyrelsen 2010). There are two  
339 sets of concentrations; the first is on a dry matter basis and the second are P related concentrations. The  
340 latter is only given for Pb and Cd of the four heavy metals of the investigation. The limiting values are  
341 shown in table 3. Soil contamination with Cd from phosphate fertilizer is a major issue. The Cd content  
342 in the salt was 0.9 mg Cd/kg, which is higher than the Danish limiting value of 0.8 mg Cd/kg (table 3).  
343 The Cd contamination level in common P fertilizers ranges from trace to 300 mg/kg of dry product  
344 (Gupta et al 2014), and thus the Cd concentration in the salt is in the lower end of fertilizers. The P related  
345 concentration in the salt was 3.7 mg Cd/kg P which was less than the limiting value. An average Cd  
346 content in European fertilizers is 138 mg/kg P (Davister 1996) and the salt contains significantly less.  
347 The total concentrations of Cu, Pb and Zn in the salt were all below the limiting values. In addition, the  
348 P related limiting value for Pb was by far met in the salt.

349

350 The concentrations of macro elements (P, Ca, Al and Fe) in the salt are shown in table 3. A SEM-EDX  
351 investigation of dry salt verified that the macro elements in the salt were only those given in the table 3.  
352 As aimed for, the salt had a very high content of P (24% per weight) and calculated to  $P_2O_5$  this  
353 corresponds to 56% per weight, which is higher than the economic grade of phosphate rock ranging from  
354 25% to 37% (Gupta et al 2014). In case evaporation is chosen as method for further processing the filtrate  
355 towards use in fertilizer, it is of importance that the water soluble fraction of P in the salt was very high  
356 (92%), which is very positive. Fe and Al phosphates are poorly soluble, and these could constitute a part  
357 of the salt, but as 66% Fe and 60% Al were in a water soluble form, less than half of these elements can  
358 be present as poorly soluble phosphates. In addition, the concentrations of Fe and Al were very low  
359 compared to that of P. On a molar basis there were 9% Al and 0.5% Fe in relation to P, so the maximum

360 loss of water soluble phosphorous compounds due to precipitation of Al and Fe phosphates would be  
361 less than 10%. The molar ratio between Ca and P in the salt was 0.17, but as both elements have high  
362 water solubility poorly soluble calcium phosphates are not formed. Calcium dihydrogen phosphate is  
363 soluble in weak acid and is the suggested form. The major part of the salt crystals is considered to be  
364 phosphoric acid crystals, which are colorless and hygroscopic crystals, exactly as experienced for the  
365 crystals formed in this project. The salt had good quality for use in fertilizer production i.e. high water  
366 solubility of P and a low concentration of heavy metals, however, full evaporation at 50°C is time and  
367 energy consuming so chemical precipitation could be a better solution. Important is though the low  
368 content of impurities in the filtrate, which allows for further processing towards fertilizer production.

369

#### 370 **4. CONCLUSION**

371 SSA was used as secondary resource for P recovery in the present investigations. SSAs from two different  
372 municipal wastewater treatment plants were included. The SSAs contained slightly less P than phosphate  
373 rock used in commercial fertilizer production and more heavy metals. Simultaneous recovery of  
374 phosphorous and separation of heavy metals from SSA was obtained in a two-compartment  
375 electrodialytic cell. The SSA was initially suspended in distilled water at the anode compartment and  
376 during application of an electric DC field, pH decreased in the suspension due to electrolysis at the anode.  
377 The acidification caused mobilization of P and heavy metals. In the applied electric field the heavy metals  
378 were transported over the cation exchange membrane into the catholyte. Higher extractions of P were  
379 obtained by EDS from both SSAs compared to chemical extraction at the same pH. A longer duration of  
380 the EDS process to reach high P extraction was needed for one of the ashes, 10 days vs. 7 days, (as it had  
381 higher buffer capacity). Recovery of 80-90% P was obtained (defined as the fraction in the solution of

the anode compartment) with less than 20% of the original heavy metals for both ashes. A P-salt was produced from the filtrate and the salt had a low content of impurities, which allows for further processing towards fertilizer production.

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	Duration (days)	Dissolved ash (%)	Final pH in suspension	Final concentrations in ash Cu/Pb/Zn (mg/kg)
A1	3	27.2	2.1	540/180/1160
A2	5	44.5	1.7	390/220/1050
A3	7	50.8	1.6	250/170/1030
A4	10	54.3	1.1	210/160/840
A5	10	53.7	1.1	260/150/950
A6	10	53.9	1.1	260/140/1010
A7	14	53.9	1.0	210/120/930
B1	5	26.2	4.3	600/120/2900
B2	7	42.8	2.1	510/140/2700
B3	10	64.7	1.2	690/140/4200
B4	14	65.5	1.0	700/140/4100
B5	16	63.7	1.1	690/130/4100

448 *Table 1: The duration and SSA varied between the experiments. Shown are also for the SSA the final pH, dissolution during*  
449 *the experiment and concentrations of Cu, Pb and Zn.*

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	Ash A	Ash B
pH (H <sub>2</sub> O)	9.6 ± 0.1	12.4 ± 0.1
Conductivity (mS/cm)	2.8 ± 0.2	10.3 ± 0.1
Loss on ignition (550°C) (%)	0.5 ± 0.05	3.0 ± 0.12
Solubility in water (g/kg)	15	66
Water soluble Cl (mg/kg)	25 ± 1	860 ± 8
P (g/kg)	110 ± 1.1	72.3 ± 2.1
Al (g/kg)	21.6 ± 0.3	14.1 ± 4.4
Zn (mg/kg)	2030 ± 14	2180 ± 65
Cu (mg/kg)	700 ± 3.6	480 ± 12
Pb (mg/kg)	115 ± 2.3	81 ± 2.5
Cd (mg/kg)	3.2 ± 0.1	2.2 ± 0.2

Table 2: Characteristics of the two investigated SSAs.

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	P	Al	Ca	Fe	Cu	Pb	Zn	Cd
Total concentration (mg/kg)	244,000	18,700	55,400	2,200	248	91	460	0.9
P related concentration (mg/kg P)					1,020	370	1,900	3.7
Soluble in water (mg/kg)	224,000	11,300	53,500	1,460	240	22	430	0.5
Water solubility (%)	92	60	97	66	97	24	94	56
Limiting value (mg/kg)					1,000	120	4,000	0.8
Limiting value (mg/kg P)					-	10,000	-	100

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*Table 3: Total concentrations, phosphorous related concentrations, water soluble concentrations and water solubility of different chemical elements in the salt produced from experiment A6. The limiting values are from (Miljøstyrelsen 2010).*

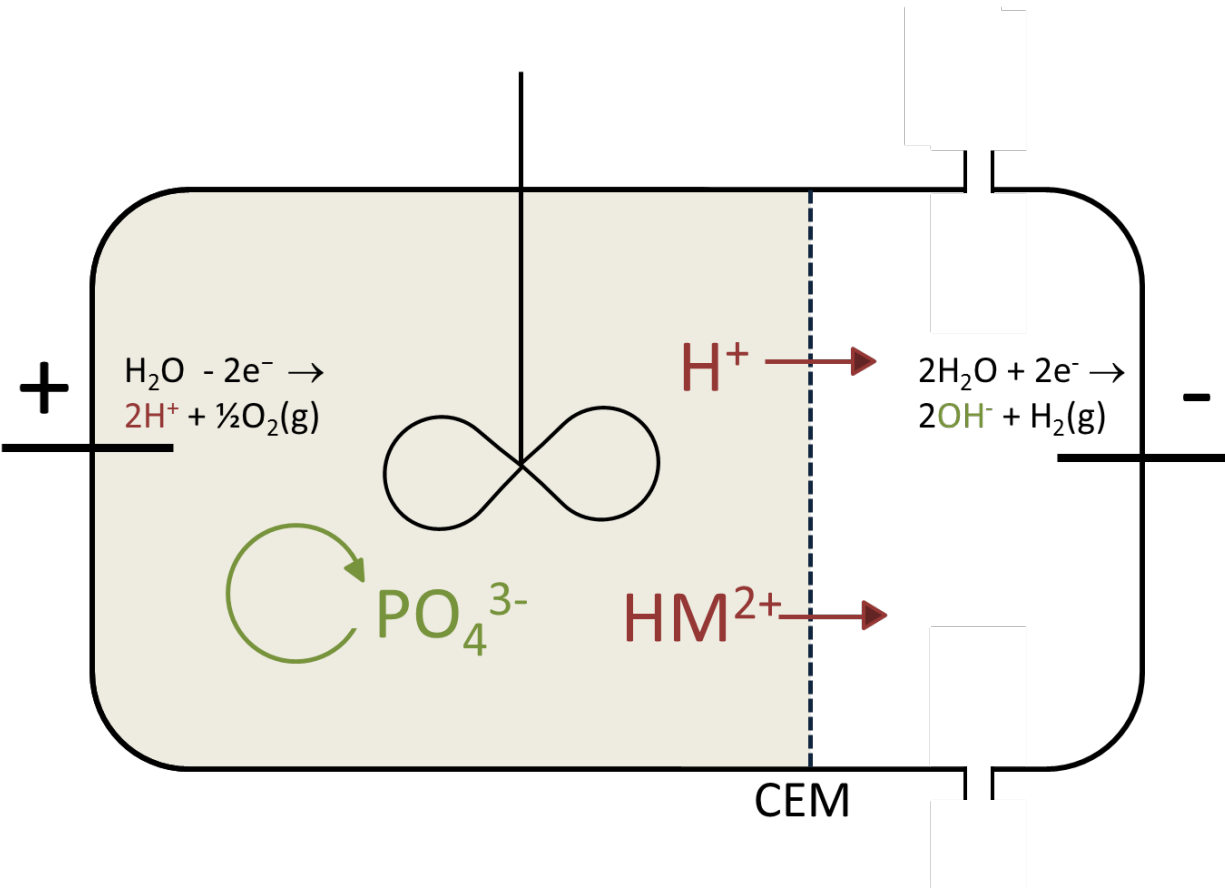
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466 *Figure 1: Two-compartment electrodialytic cell for simultaneous P recovery and heavy metal separation from*  
467 *sewage sludge ash. The compartments are separated by a cation exchange membrane (CEM). The ash is*  
468 *suspended in water in the anode compartment. During the application of current, the suspension is acidified*  
469 *from electrolysis at the anode (reaction shown in the figure). In the acidic environment the P and heavy metals*  
470 *are brought into solution and the heavy metal cations ( $\text{HM}^{2+}$ ) are transported into the catholyte by*  
471 *electromigration.*

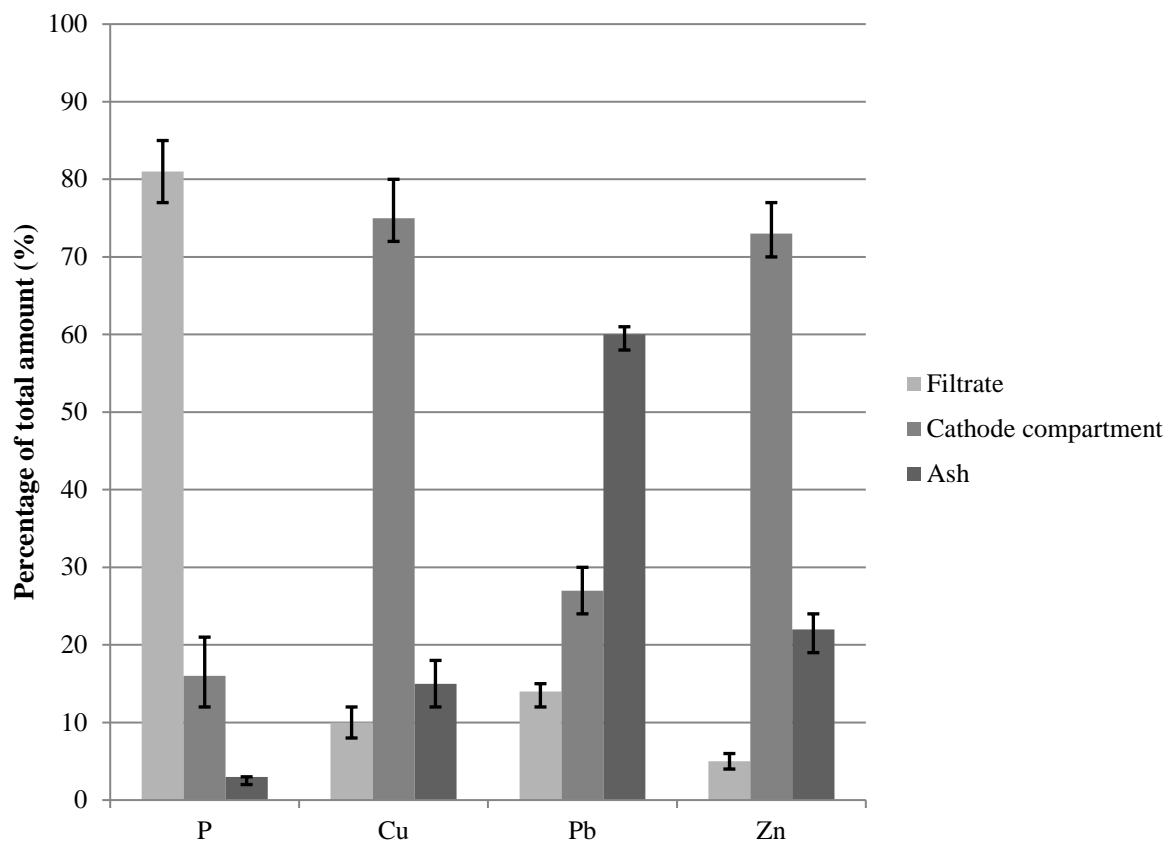


Figure 2: Repeatability of phosphorous and heavy metal distribution at the end of three similar experiments (A4-A6). Mean values are shown in solid bars and the error bars shows minimum and maximum values.

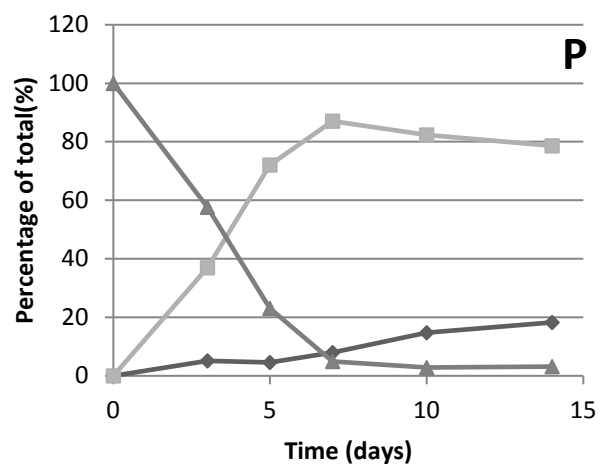
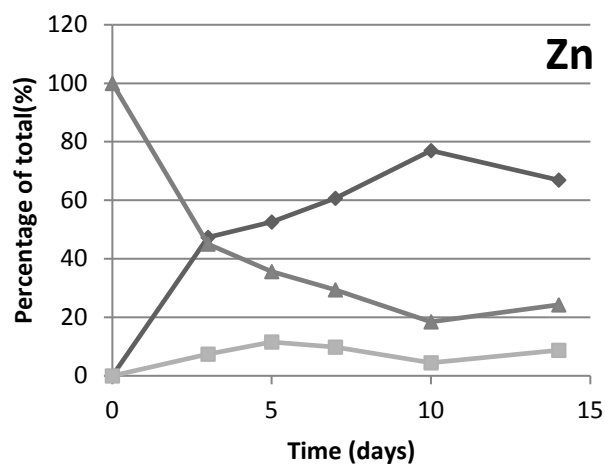
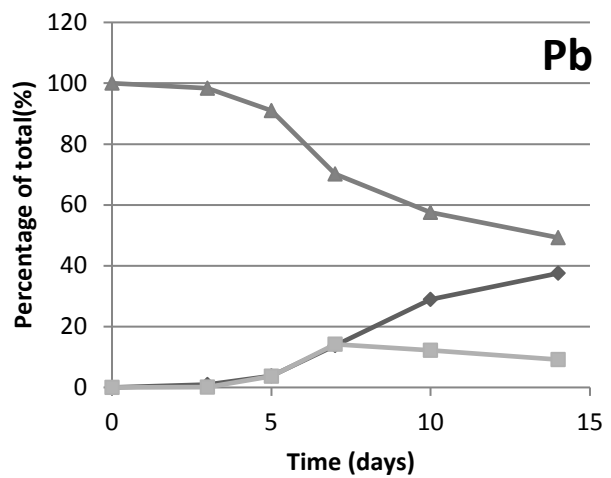
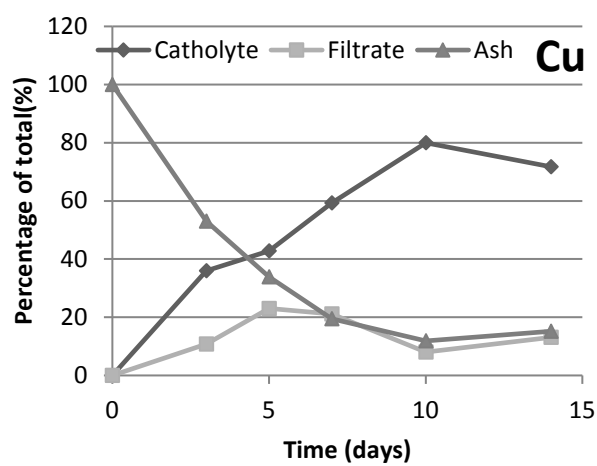


Figure 3: Distribution of Cu, Pb, Zn and P in the two-compartment cell over time for Ash-A

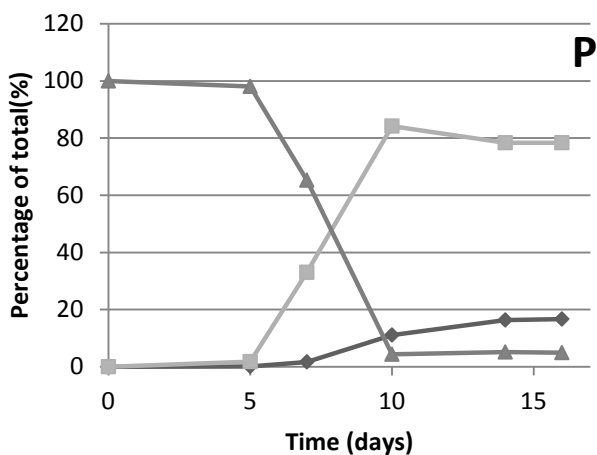
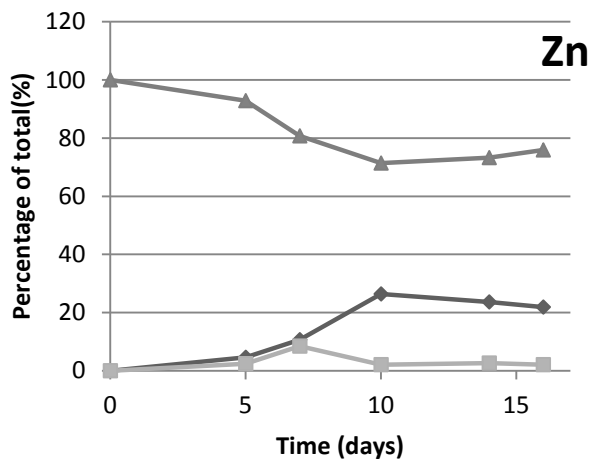
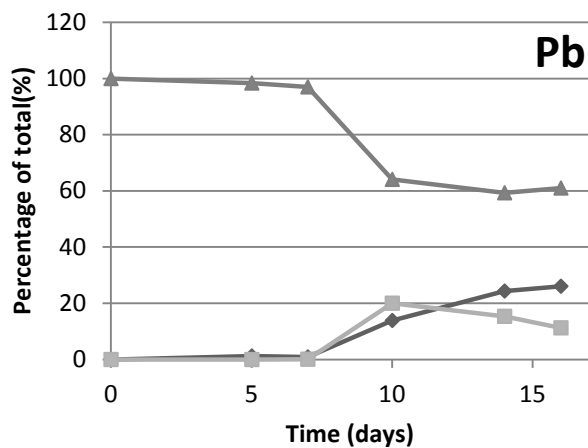
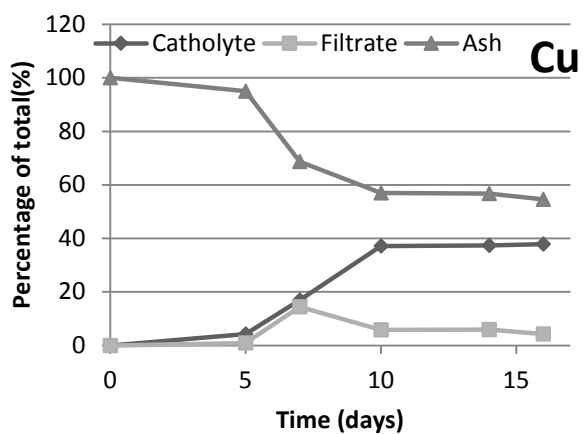


Figure 4: Distribution of Cu, Pb, Zn and P in the two-compartment cell over time for Ash-B